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Relationships between Direction of Wind Flow and Ozone Inflow Concentrations at Rural Locations Outside of St. Louis, Missouri

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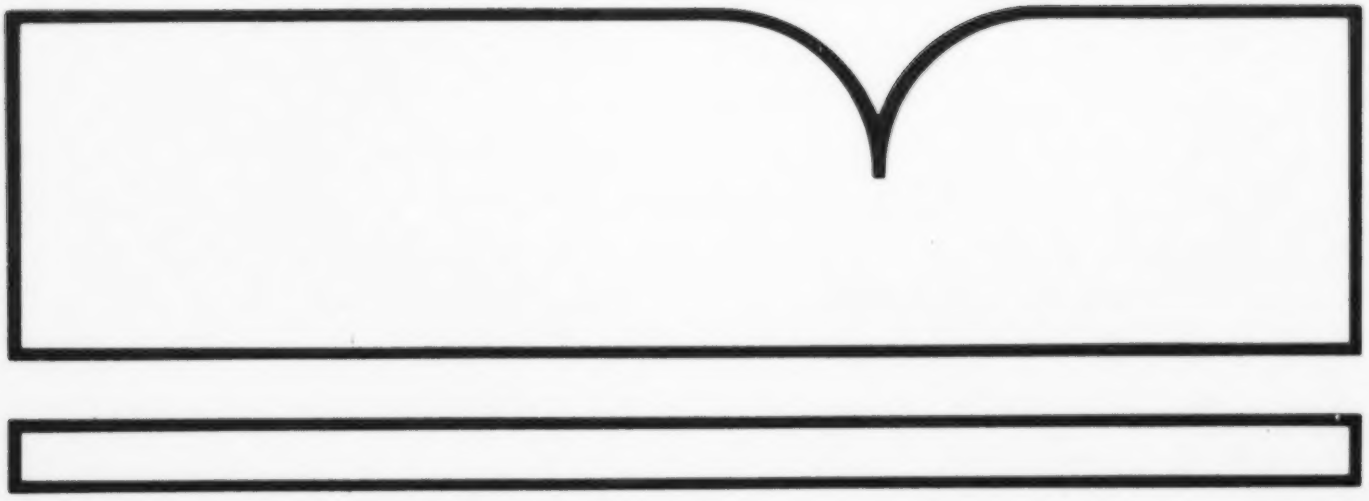

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16. ABSTRACT

The relationships between the monthly averages of daily 1200-1500 h O_3 inflow concentrations and the wind flow direction are evaluated using measurements at rural locations outside of St. Louis, MO. The results obtained are consistent with the O_3 gradients obtained from other monitoring studies of O_3 at rural locations west and east of St. Louis. Although there may be a stratospheric component to these ground level rural O_3 concentrations most of the O_3 measured can be associated with photochemical O_3 formation in the free troposphere and in the boundary layer. Most of the gradient in rural O_3 concentrations from west to east of St. Louis is attributed to higher anthropogenic emissions of O_3 precursors to the east rather than to differences in meteorological conditions from west to east.

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RELATIONSHIPS BETWEEN DIRECTION OF WIND FLOW AND OZONE INFLOW CONCENTRATIONS AT RURAL LOCATIONS OUTSIDE OF ST. LOUIS, MO

A. P. ALTSHULLER

Atmospheric Sciences Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, U.S.A.

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Abstract—The relationships between the monthly and seasonal averages of the daily 1200–1500 h O_3 inflow concentrations and wind flow direction have been evaluated. The O_3 measurements used are those during inflow of air parcels from upwind to rural monitoring stations outside of St. Louis, MO. The results obtained are consistent with the O_3 measurements reported from other monitoring studies at rural locations both to the west and east of St. Louis. Although there is a stratospheric component to these ground level rural O_3 concentrations, it is likely that most of the O_3 measured during the warmer months of the year is associated with photochemical O_3 formation in the planetary boundary layer and in the free troposphere. A substantial part of the increments in rural O_3 concentrations which occur from west to east of St. Louis during the warmer months of the year appear best to be accounted for as a result of photochemical formation O_3 precursors from anthropogenic emission sources to the east of St. Louis. Differences in the values of meteorological parameters with wind flow direction account for only a small part of the differences in O_3 concentration observed.

Key word index: Ozone, nitrogen oxide, photochemical, wind direction, planetary boundary layer, free troposphere, stratosphere, anthropogenic emissions, biogenic emissions.

INTRODUCTION

Ozone measurements are among the air quality measurements made at 25 urban and rural stations of the Regional Air Monitoring System (RAMS) during the Regional Air Pollution Study (RAPS) in the St. Louis, MO area. Several previous investigations have used the O_3 measurement data base to relate O_3 concentrations to other air quality measurements and to meteorological parameters (Altshuller, 1985; Karl, 1978a,b, 1979, 1980; Shreffler and Evans, 1982).

An improved understanding of the relationships between direction of wind flow and O_3 inflow concentrations should be useful in evaluating the potential for adverse effects of O_3 on field crops and forests (Heck *et al.*, 1984; U.S. Environmental Protection Agency, 1984a). Inflow O_3 concentrations, 1200–1500 h CST, have been calculated from the O_3 measurements at the four outermost rural stations in RAMS (Shreffler and Evans, 1982). This set of O_3 statistics can be utilized to examine the influence of direction of wind flow on the variations in inflow concentrations of an area in mid-continent.

In the present study the monthly and seasonally averaged O_3 inflow concentrations are related to direction of wind flow by quadrant. These O_3 inflow concentrations are compared especially for E and W wind flows. The O_3 concentrations in the St. Louis area are compared to those measured at other rural locations in adjacent regions of the U.S. during recent years. The extent to which differences in O_3 inflow concentrations between wind flow directions are accounted for by other meteorological parameters is evaluated. The various processes affecting O_3 formation are considered as they may account for the results obtained.

PROCEDURE

A data compilation already available based on the O_3 measurements at the four outermost rural stations in the St. Louis RAPS network is utilized (Shreffler and Evans, 1982). These investigators calculated an O_3 inflow concentration measured at up to three rural stations within the upwind flow between 1200 and 1500 h CST. This approach was selected to stabilize the O_3 concentration statistics for upwind flows by use of the (up to) 12 1-h average O_3 concentrations available to form these 1200–1500 h CST averages each day.

In this work these 1200–1500 h O_3 concentrations for each day of all months in 1975, 1976 and in the first quarter of 1977 are stratified by the quadrant from which the average daytime flow occurs. The NE, SE, SW and NW quadrants are associated with flows from 0.0° to 89.9°, 90.0° to 179.9°, 180.0° to 269.9° and from 270.0° to 359.9°. The wind data are obtained from the measurements at 25 RAPS monitoring stations taken either at 10 m or 30 m heights. Values are weighted somewhat towards those obtained in central city locations because of the higher density of stations

there. The wind vector each day is an indication of the net drift of the mesoscale air mass during the 0700–1359 h CST period (Shreffler and Evans, 1982).

Evaluations of the statistical significances for the differences in monthly and quarterly mean concentrations of inflow O_3 concentrations were carried out by analysis of variance and the Wilcoxon 2-sample test. Probability values in almost all instances were very nearly the same from these tests.

In the comparisons of the O_3 concentrations measured in various other studies, the 1200–1500 h O_3 concentrations can usually be calculated from tabulated hourly average O_3 concentrations or from plots of averaged diurnal O_3 patterns. In other studies the maximum 1-h O_3 concentrations are often reported. Based on the diurnal O_3 patterns from a number of studies the O_3 profiles at rural locations are almost flat during the afternoon (Decker *et al.*, 1976; Evans *et al.*, 1983; Research Triangle Institute, 1975; Shreffler and Evans, 1982). The 1200–1500 h O_3 concentrations average only slightly lower values than the 1-h maximum O_3 concentrations. Therefore the 1200–1500 h O_3 concentrations can be closely approximated.

In the RAPS study the O_3 gas-phase chemiluminescence monitors were calibrated by gas-phase titration with NO. Other O_3 measurement studies to be considered used neutral buffered KI (Decker *et al.*, 1976; Pratt *et al.*, 1983; Research Triangle Institute, 1975) as the calibration method or the ultraviolet photometer (Kelly *et al.*, 1982; Shaw and Paur, 1983) for calibration. Adjustment for differences in calibration technique have been discussed, especially between those O_3 measurements based on the NBKI calibration and those based on the other calibration techniques (U.S. Environmental Protection Agency, 1984b). However the O_3 concentrations measured at rural locations are rarely high enough to necessitate such adjustments. No adjustment between measurements of O_3 calibrated by ultraviolet photometry and gas-phase titration appears necessary (U.S. Environmental Protection Agency, 1984b).

To evaluate the possible interactions of other meteorological parameters with wind direction it is necessary to adjust the O_3 concentrations stratified by wind quadrant to the same values of temperature, wind speed and solar radiation intensity. The approach taken is to place the daily 1200–1500 h O_3 concentrations into cells associated with selected ranges of these meteorological parameters. The ranges selected are ± 2°C, ± 0.5 m s^{-1} and ± 0.2 ly m^{-1}. For example, one cell will contain the O_3 concentrations for those days for which the daily average values, 0700–1359 CST, of temperature are in the range between 24.0° and 27.9°C, of wind speed between 2.0 and 2.9 m s^{-1} and of solar radiation intensity in the range between 0.80 ly m^{-1} and 1.20 ly m^{-1}. These intervals are selected to permit substantial resolution and yet include a significant number of days in each cell. An averaged 1200–1500 h CST O_3 concentration is obtained for each cell from the individual O_3 concentrations for the group of days falling within each cell. Plots of these averaged O_3 concentrations from each of these cells were prepared to obtain the variations of the cell averaged O_3 concentrations with changes in one of the three meteorological parameters, while the other meteorological parameters are maintained at appropriate fixed values within the experimental ranges of these parameters. Using this group of plots the averaged O_3 concentrations for paired sets of days stratified by wind direction are adjusted by interpolations made within these plots to the O_3 values corresponding to the same average temperature, wind speed and solar radiation intensity.

RESULTS

The monthly mean 1200–1500 h CST O_3 inflow concentrations associated with wind flows from upwind of the St. Louis area are given in Fig. 1. These O_3 inflow concentrations increase rapidly from the winter into the spring and summer. Peak concentrations occur during the months of June, July or August. These peak concentrations are followed by rapid decreases in O_3 inflow concentrations during the fall.

The monthly mean 1200–1500 h CST O_3 inflow concentrations associated with wind flows from the E or W are also given in Fig. 1. The number of days associated with flows from the E, especially the NE, are small during several of the months during late 1976 and early 1977. The number of days associated with flow from the E is so small during November 1976 as to make it necessary to delete the value for this month from Fig. 1.

Higher monthly mean O_3 inflow concentrations are associated with wind flows from the E compared to the W during April–August 1975 and May–October 1976 excepting August. The differences in these means are statistically significant ($P \leq 0.05$) for the months of April–July 1975 and for June and September 1976. For the months of May and July 1976 probability values of slightly above 0.1 are associated with the differences in the means. Higher monthly mean O_3 inflow concentrations are associated with wind flows from the W during January–March 1975, December 1975–March 1976 and December 1976–March 1977. The differences in these means are statistically significant only for months within the first quarters of 1975 and 1976. The peak monthly mean O_3 inflow concentrations with wind flows from either the E or W occur in June, July or August with no secondary peaks evident during other seasons of the year. Plots (not shown) of monthly mean O_3 inflow concentrations when wind flows occur from the NE, SE, SW and NW quadrants show similar patterns to those in Fig. 1. Peak monthly mean O_3 concentrations also occur during the months of June, July or August. Monthly mean O_3 inflow concentrations averaged over those days when wind flows are from the NE or SE fall into the 80–89 ppb range during the months of June and July 1975 and May, June and August 1976.

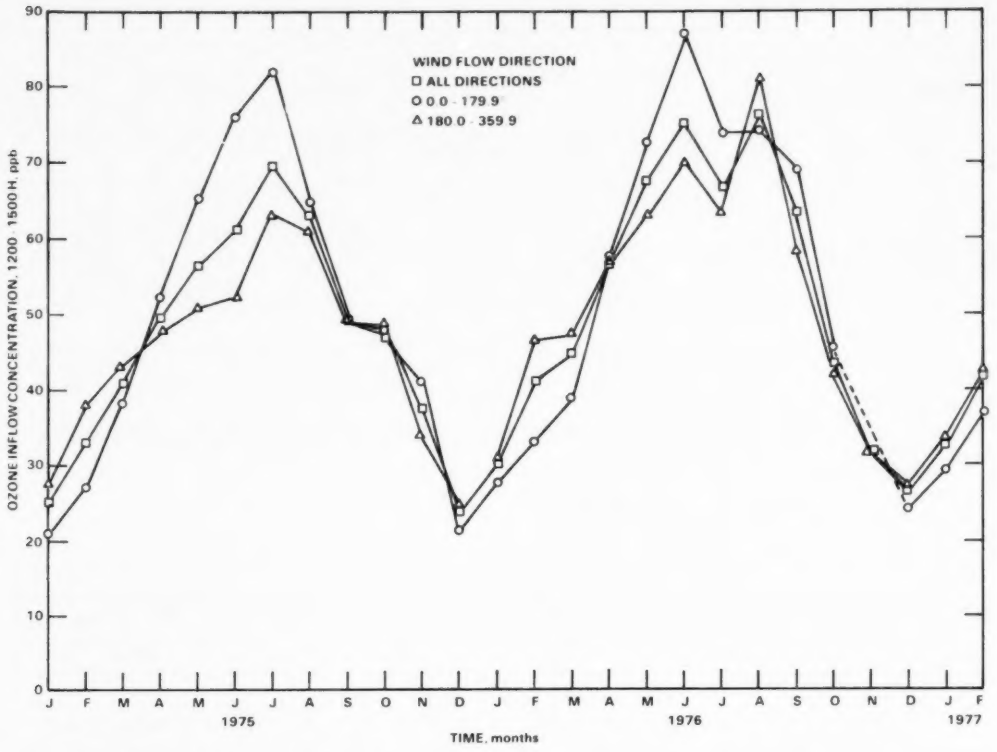

Fig. 1. Monthly means in the 1200–1500 h O_3 inflow concentrations from upwind into the St. Louis area during 1975, 1976 and 1977, associated with wind flows from (a) all directions, (b) the East and (c) the West.

The monthly mean O_3 inflow concentrations can be considered in relation to the distribution of daily average 1200–1500 h inflow concentrations $\geqslant 80$ ppb. Forty-six of the 72 days when these O_3 concentrations are reached in 1975 and 1976 occur during the months of June and July 1975 and May, June and August 1976. Daily O_3 inflow concentrations $\geqslant 80$ ppb, $\geqslant 90$ ppb and $\geqslant 100$ ppb are associated with wind flows from the E on 60%, 68% and 80% of these days in 1975 and 1976. By wind flow quadrant the number of days associated with these higher O_3 inflow concentrations are in the order SE > NE $\geqslant$ SW $\geqslant$ NW.

The quarterly mean 1200–1500 h CST O_3 inflow concentrations and standard error of means are tabulated in Table 1 as associated with wind flows from the NE, SE, E, SW, NW and W. Higher quarterly mean O_3 inflow concentrations occur when the wind flows are from the NE or SE rather than from the NW during the second and third quarters of 1975 and 1976. For several quarters the difference in these mean values are statistically significant (Table 1). During the first and fourth quarters the averaged O_3 inflow concentrations are usually higher when the wind flows are from the SE compared to the NE and from the SW compared to the NW ($P \leqslant 0.02$). During the first quarter of 1975 the higher averaged O_3 inflow concentrations occur when flow is from the NW rather than the SW; however, the difference in means is not statistically significant.

DISCUSSION

Several of the directional aspects of wind flow on O_3 concentrations considered here have been discussed previously based on results at other midwestern locations in the U.S. Ludwig and coworkers (1977), based on air-parcel travel directions to four midwestern monitoring sites, observed that the frequency of occurrence of higher O_3 concentrations increased substantially when the air-parcel travel directions shifted from NW to SW. Similarly, Viezee and coworkers (1982) based on measurements near Pierre, SD (Kelly *et al.*, 1982) also observed that higher O_3 concentrations were associated with wind flows from the SW than from the NW. Pratt and coworkers (1983) reported that O_3 concentrations measured at three rural locations in Minnesota and N Dakota were slightly higher when the wind flow was from the E rather than the W. Therefore, the present results on directional effects on O_3 concentration are qualitatively consistent with these earlier observations.

The O_3 measurements of Decker and coworkers (1976) are consistent with the O_3 inflow concentrations

Table 1. Quarterly mean concentrations, standard error of means and number of daily values for inflow ozone concentrations by wind flow direction into the St. Louis area

Quarter	Year	Ozone inflow concentration, 1200–1500 h, in ppb NE	SE	E	SW	NW	W
1st	1975	29.0,2.72,15	29.6,3.19,20	29.4,2.14	32.7,2.44,21	37.4,2.15,30	35.5,1.63
2nd*	1975	68.5,4.84,16†	55.9,2.71,22†	61.2,2.73‡	52.0,1.82,33	49.2,2.49,17	51.0,1.47
3rd*	1975	70.1,6.03,15†	59.3,4.17,21	63.8,3.56	60.0,3.54,27	55.5,4.18,27	57.8.2.73
4th	1975	27.8,6.35,11	40.5,2.81,31§	37.2,2.76	41.1,3.86,29§	25.4,2.12,20	34.7,2.67
1st	1976	26.8,2.46,7	35.7,2.11,23§	33.6,1.84	44.9,2.24,25§	37.5,1.75,33	40.7,1.46
2nd*	1976	65.6,4.52,18	73.2,4.07,24	69.9,3.05	63.9,3.04,32	64.3,5.67,16	64.1,2.74
3rd*	1976	65.3,3.40,22	80.1,3.33,20†	72.4,2.62‡	66.6,3.01,26	61.9,3.63,20	64.5,2.32
4th	1976	29.3,3.67.8	44.7,7.70,11	38.2,4.95	36.5,2.87,34§	28.8,1.41,38	32.4,1.60
1st	1977	24.3,2.20,2	41.3,3.01,22	39.9,2.93	45.4,2.49,21§	37.9,0.97,41	40.4,1.14

* The larger mean O_3 concentrations for each quadrant during the second or third quarters compared to those for the same quadrants during the first or fourth quarters are statistically significant, P at least 0.01 and usually with $P \leq 0.001$.

† The larger mean O_3 concentrations with wind flows from the NE or SE compared to those from the NW are statistically significant, $P \leq 0.08$.

‡ The larger mean O_3 concentrations with wind flows from the E compared to the W are statistically significant, $P \leq 0.03$.

§ The larger mean O_3 concentrations with wind flows from the SE compared to NE and the SW compared to NW during the first or fourth quarters are statistically significant, $P \leq 0.04$.

into the St. Louis area with respect to the peaking in concentrations during the summer of 1975. The highest values of their monthly average O_3 concentrations occur usually during the months of July or August at a considerable number of urban and nonurban locations in the midwestern U.S.

Hourly average measurements of O_3 concentrations, obtained during the third quarter of 1975 at four rural locations well to the E or W of the St. Louis area (Decker *et al.*, 1976), have been used to calculate the 1200–1500 h O_3 concentrations shown in Table 2. These values for O_3 concentrations at these four locations indicate increments from the NW to NE ranging from 8 to 16 ppb averaged over the third quarter of 1975. During the same season the average 1200–1500 h O_3 inflow concentration, from downwind into the St. Louis area from the NE, of 70 ppb was 15 ppb higher than for inflow from the NW (Table 1) and the difference in means is statistically significant, $P = 0.05$.

Similar results have been obtained from O_3 measurements made the previous summer at five nonurban sites E of the St. Louis area (Research Triangle Institute, 1975). The third quarter mean 1400 CST O_3 concentrations during 1980 have been calculated for three midwestern nonurban sites from the monthly averaged values (Shaw and Paur, 1983). These results are given in Table 2.

Table 2. Averaged midday ozone concentrations from measurements made at nonurban locations during summer periods

Reference	Measurement period	Site	Location/alt. (m)MSL	O_3 concentration, ppb, 1200–1500 h CST
Research Triangle Inst., 1975	14-6-74 to 31-8-74	Wilmington	sw OH/403	68
		McConnelsville	se OH/305	64
		Wooster	me OH/346	65
		McHenry	w MD/884	61
		DuBois	w Central PA/554	71
Decker *et al.*, 1976	27-6-75 to 31-9-75	Bradford	nw PA/653	53
		Lewisburg	se WV/702	56
		Creston	sw IA/394	45
		Wolf Point	ne MT/605	40
Kelly *et al.*, 1982	13-7-78 to 6-9-78	40 km wnw Pierre	nw SD/500	38
Pratt *et al.*, 1983	1-7 to 30-9 1977–1981	Traversse Co.	w central MN/NR*	43
		La Moure CO	se ND/NR*	40
Shaw and Paur, 1983	1-7-80 to 30-9-80	Union Co	w KY/NR*	70†
		Franklin Co	se IND/NR*	60†
		Ashland Co	ne OH/NR*	55†

* Not reported but less than 1000 m based on terrain in area.

† 1400 h CST.

Vukovich and coworkers (1985) constructed O_3 isopleths of mean diurnal maximum O_3 concentrations for the U.S. E of 100° W longitude. These isopleths were based on measurements of O_3 at rural locations during August for the years 1977–1981. The mean O_3 concentration is 40 ppb near an isopleth passing through Wisconsin, Minnesota, northwestern Iowa into northern Nebraska. The mean O_3 concentration was at or somewhat above 60 ppb for an isopleth passing to the NE and SE of the St. Louis area, as well as immediately to the SW of St. Louis.

All of these results are consistent with significant increments in the O_3 concentrations measured during the summer months from W to E, and especially from NW of the St. Louis area to NE of this area. In addition an increment in the O_3 concentrations with flows from SE or SW compared to NW of the St. Louis area is reported in some of the studies.

Comparison of O_3 concentrations at locations far to the NW of St. Louis with the O_3 concentrations in the inflow into St. Louis from the NW also suggests incremental O_3 formation is occurring during transport eastward over relatively lightly populated terrain W of St. Louis. To examine this possibility in more detail additional O_3 measurements obtained during later time periods at locations in the upper midwestern and western United States can be evaluated.

Based on the diurnal O_3 pattern obtained at a rural site in S Dakota during July–September 1978 (Kelly *et al.*, 1982) an average 1200–1500 CST O_3 concentration of 38 ppb is obtained (Table 2).

Based on the monthly average O_3 concentrations (all h values) of Pratt and coworkers (1983), the third quarter average O_3 concentrations at the rural sites in Traverse CO, MN and La Moure CO, ND during 1977–1981 were 33 and 31 ppb, respectively. Using the annual average diurnal O_3 patterns provided by these investigators the corresponding 1200–1500 h O_3 concentrations are calculated (Table 2).

The 1200–1500 h O_3 concentrations during summer periods for the five rural locations well to the NW of St. Louis listed in Table 2 are from 10 to 24 ppb less than the corresponding O_3 concentrations with NW flow into rural locations immediately upwind of St. Louis (Table 1). These additional O_3 results included in Table 2 are consistent with significant incremental O_3 formation during flow of air masses from the NW into the St. Louis area.

The O_3 measured at rural locations during the warmer months of the year can be attributed to contributions from a varying combination of the following processes: (1) transport of O_3 formed in the stratosphere down to ground level, (2) transport of O_3 formed by *in-situ* photochemistry in the free troposphere down to ground level, (3) local O_3 formation by photochemistry from HC and/or NO_x emitted from natural sources, (4) local O_3 formation by photochemistry from HC and NO_x emitted from anthropogenic sources, (5) O_3 formed photochemically in individual plumes especially within one-days transport distance, (6) O_3 formed photochemically from HC and NO_x undergoing multiday transport. Processes (3) to (6) are considered to be occurring within the planetary boundary layer. In most instances the tracer materials measured are inadequate to discriminate clearly among these contributions. Mixing of O_3 and other constituents occurs between the planetary boundary layer and the rest of the troposphere as a result of such additional processes as the frontal downdrafts associated with cold fronts, thunderstorm updrafts and downdrafts, as well as the updrafts and downdrafts associated with cumulus cloud activity (Alkezweeny and Ching, 1986; Ching *et al.*, 1984; Greenhut *et al.*, 1984; Viezee *et al.*, 1983).

Stratospheric O_3 as a contributor to surface O_3 concentrations

Tropopause folding events appear to be the dominant process by which O_3 formed in the stratosphere is injected into the free troposphere (Danielsen and Mohnen, 1977; Viezee *et al.*, 1979). These events are associated with the occurrence of 500-mb low pressure troughs. The O_3-rich air parcels from the stratosphere tend to bend over into nearly horizontal layers well aloft in the free troposphere (Johnson and Viezee, 1981). Unless appropriate meteorological conditions occur concurrently, resulting in rapid transport of O_3 to the surface (Johnson and Viezee, 1981), the O_3 in such air parcels can react and be diluted by tropospheric air over extended periods before reaching the surface. Rapid transport of stratospheric O_3 to the surface occurs infrequently, based on episodic studies in the literature (Viezee *et al.*, 1983). Because of these complexities the surrogate species ^{90}Sr and ^{7}Be also formed in the stratosphere and attached to particles are often used in discussions of stratospheric contributions to surface O_3 concentrations (Altshuller, 1986).

Estimates made of the annual average contribution of O_3 produced in the stratosphere to surface O_3 concentrations based on surface ^{90}Sr concentration measurements and other evidence range from 7 to 15 ppb (Mohnen and Reiter, 1977; Reiter, 1978; Viezee *et al.*, 1979). The higher values in this range have not been corrected for surface losses of O_3 (Viezee *et al.*, 1979).

Seasonal variations in the frequency of 500-mb low pressure troughs and in surface ^{7}Be concentrations with latitude and longitude have been discussed (Viezee *et al.*, 1982). Correlation coefficients between the occurrence of 500-mb low pressure troughs and ^{7}Be concentrations average near 0.7, while correlation coefficients between surface ^{7}Be concentrations and O_3 concentrations range between 0.5 and 0.7 (Johnson and Viezee, 1981; Kelly *et al.*, 1982; Viezee *et al.*, 1982). Quantitative estimates of the contributions of stratospheric O_3 undergoing rapid transport downward to O_3 concentrations measured at the summit of Whiteface Mt., NY, by a procedure based on ^{7}Be measurements, result in an average estimated strato-

spheric contribution of about 50% on 11 out of 26 days during June and July 1977 (Dutkiewicz and Husain, 1979).

None of these results can be used to make quantitative estimates of the seasonal contributions of stratospheric O_3 to surface O_3 concentrations within geographic regions of the United States. It is doubtful that adequate estimates can be made in view of the differing influences of the processes of reaction and removal of O_3 compared to particles within the free troposphere.

The Geophysical Fluid Dynamics Laboratory general circulation/transport model has been applied to the contribution of stratospheric O_3 to troposphere O_3 concentrations (Levy *et al.*, 1985). No chemistry is included in this model either for the free troposphere or lower stratosphere. There are 'major disagreements' between predicted and observed values of O_3 at rural surface sites as well as in the free troposphere. Observed seasonal patterns are not simulated satisfactorily. The late winter or spring peaks in surface O_3 concentrations predicted for mid-latitude sites at Wallops Island, VA, Niwot Ridge, CO and Hokenpeissenberg, Switzerland are in disagreement with observed results.

The observed monthly mean patterns of O_3 inflow concentrations into the St. Louis area, irrespective of wind flow direction, do not show evidence of the spring maximum predicted at mid latitudes in the northern hemisphere if stratospheric O_3 is the source of the surface O_3 concentrations (Levy *et al.*, 1985).

Free tropospheric O_3 formation as a contributor to surface O_3 concentrations

A considerable number of modeling studies have been concerned with the chemistry of O_3 formation in the free troposphere. Developments in this field have been reviewed (Fishman, 1984). In the present discussion modeling scenarios concerned with estimating the effects of O_3 formation of surface emissions of HC and NO_x are of particular interest.

Fishman and Seiler (1983) calculated the distribution of O_3 in a tropospheric column from a photochemical model with and without the inclusion of a surface source of NO_x. In the absence of a surface source of NO_x emissions, but with downward fluxes of O_3 and NO_y from the stratosphere and a tropospheric source of NO from lightning, the O_3 concentration calculated at 1 km is 15 ppb. Inclusion of a weak background surface source of NO_x resulted in an increase of the predicted O_3 concentration by 20 ppb up to 35 ppb at 1 km under July conditions at 40° N latitude.

The one-dimensional model subsequently was modified to include the chemistry of non-methane HCs with NO_x, as well as to parameterize mixing processes in the planetary boundary layer (Fishman and Carney, 1984). The background non-methane HC concentration in the boundary layer was estimated at 6 ppbC and the ground-level NO_x concentration derived is about 0.25 ppb. The predicted midday O_3 concentration at 1 km increased by 6 ppb and an O_3 concentration of slightly below 40 ppb is predicted to occur at ground level.

Photochemical formation of O_3 within the planetary boundary layer

Anthropogenic emission inventories by county in the U.S. have been compiled for volatile organic compounds, VOCs and NO_x for the late 1970s (U.S. Environmental Protection Agency, 1984b). The strongest source emission areas are to the NE of the St. Louis area, but substantial source emission areas also occur to the SE of St. Louis. Immediately to the W of St. Louis these emissions decrease somewhat, but are still substantial. However the emissions of VOCs and NO_x decrease to low levels > 500 km to the W of the St. Louis area. The only large area source within 400–500 km to the W is the Kansas City area. Far to the SE strong sources of VOCs and NO_x emissions occur from eastern Texas.

Higher emission densities of biogenic organic emissions are expected at lower latitudes (25°N–35°N) compared to higher latitudes (40°N–50°N) and to the SE rather than the SW (Altshuller, 1983). However direct experimental evidence demonstrating a contribution from biogenic emissions to O_3 formation and surface O_3 concentrations is unavailable.

Estimates of the potential contribution of biogenic organic emissions to O_3 formation have been made by two procedures (Altshuller, 1983). Ambient air measurements of the composition and concentrations of organic compounds can be combined with estimates of the O_3 forming potential of biogenic organics compared to anthropogenic organics based on laboratory photochemical irradiation experiments. The second approach is to incorporate various biogenic emission inventories into photochemical modeling scenarios.

At the VOC:NO_x ratios reported in rural areas, the O_3 forming potential of the biogenic organics such as isoprene and terpenes is equal to or less than that of anthropogenic HCs (Altshuller, 1983). The ambient air measurements indicate that less than 10% of the VOCs can be identified as biogenic organics. Combining these results the typical contribution of biogenic organics to the formation of rural O_3 concentrations is estimated as 1 ppb or less (Altshuller, 1983). However, during periods of strong local air stagnation it is estimated that biogenic emissions may contribute as much as 2–10 ppb to the O_3 concentrations observed.

Modeling studies after including biogenic organics in their emission inventories usually predict increases in O_3 concentrations of 10% or less (Altshuller, 1983). In instances where substantial contributions to O_3 formation biogenic organics have been predicted the modelers have had to assume biogenic organic emission rates well above those consistent with the observed ambient concentrations.

In general it has been possible to predict under

realistic ambient conditions only small contributions to O_3 concentrations attributable to the presence of biogenic organics. The high photochemical reactivities and short lifetimes of the biogenic HCs (Altshuller, 1983) also greatly limit their contribution to O_3 formation during long range transport within the planetary boundary layer or in the free troposphere.

There are only a few cases in which distant urban plumes have been identified as contributing to elevated O_3 concentrations at rural sites in the vicinity of St. Louis (Ellestad, 1980; Karl, 1978a; Rasmussen *et al.*, 1977). These results do not provide adequate evidence for individual urban plumes impacting the inflow into these rural sites with sufficient frequency to make a substantial contribution to seasonal or monthly average O_3 concentrations. Even less information is available on any possible impact of other types of distant large individual plumes on O_3 concentrations in the St. Louis area.

The observed differences in O_3 inflow concentrations with direction of wind flow (Fig. 1, Table 1) are generally consistent with the regional patterns in the anthropogenic emission densities of VOCs and NO_x discussed above. This is especially so for the higher episodic inflow O_3 concentrations measured in the St. Louis area (Altshuller, 1985). The frequent passage of warm high pressure systems past St. Louis to the E result in anticyclonic flows which can bring emissions originating in the NE quadrant into the St. Louis area through the SE or SW quadrants. Flow through the emission areas to the SE of St. Louis augment precursors originating in the NE which have been depleted in the formation of O_3. Karl (1978a) examined 15 selected days during the summer of 1975 and during May and June 1976 when maximum h O_3 inflow concentrations exceeded 80 ppb. He found on 13 of 15 days that the air entering the St. Louis area was dominated by slow passage of high pressure systems to the E of St. Louis during about three days prior to air arriving in the St. Louis area.

The photochemical model discussed earlier has been utilized with a much higher surface emission flux assumed corresponding to the average emission density over the eastern United States (Fishman *et al.*, 1985). After operating the model for several days of reaction time the predicted ground level O_3 concentration in mid-afternoon is about 75 ppb. After the surface emissions are shut off the O_3 concentration at 1 km is maintained near peak concentration levels for about two more days. The model-derived ground level NO_x concentration after four days of integration is about 5 ppb. This NO_x concentration is within the observed ranges of NO_x concentrations at non-urban sites in the eastern U.S. (Altshuller, 1986).

It is of use to estimate the amount of O_3 produced photochemically in ppb per ppb of NO_x at ground level. The modeling result of Fishman and Carney (1984) discussed in an earlier section predicts ~ 38 ppb of O_3 produced with 0.25 ppb of NO_x present. Assuming linearity, the ratio of O_3 produced to NO_x present over the NO_x concentration range between 0.25 ppb and 5 ppb would be near 8. Empirical calculations of this ratio based on summer ambient air measurements for a 4-h midday period results in the following ratios at three rural locations: (1) in S Dakota, 7; (2) in Virginia, 7; (3) in Louisiana, 5 (Kelly *et al.*, 1984). Another empirical calculation based on urban plume measurements of O_3 and NO_x for flow over the ocean resulted in ratios ranging from 5 to 12 (Altshuller, 1986).

Based on the estimates above, the observed third quarter seasonal difference in 1975 for O_3 of 15 ppb associated within flow from the NE compared to NW quadrant into St. Louis need be associated with differences in available NO_x concentrations of only 2–3 ppb if due to the photochemical formation of O_3. Similarly the largest monthly difference in mean O_3 concentrations of 33 ppb during June 1975 between inflows from the NE compared to the NW quadrant into St. Louis may be associated with differences in available NO_x concentrations of 4–6 ppb if due to photochemical formation of O_3.

Effects of meteorological parameters on O_3 formation within the planetary boundary layer

A number of meteorological parameters including temperature, solar radiation intensity and composition, wind speed and mixing height can influence the formation of O_3 in the boundary layer (Altshuller, 1975; Bach, 1975; Demerjian *et al.*, 1980; Holtzworth, 1972; Jeffries *et al.*, 1976; Korshover, 1975; Leighton, 1961; U.S. Environmental Protection Agency, 1978, 1984b). Empirical results of Shreffler and Evans (1982), as well as several modeling studies (Evans, 1979; Schere and Shreffler, 1982; Shreffler and Schere, 1982) involving St. Louis RAPS measurements, show substantial effects of local meteorological parameters on O_3 formation within the urban area as well as on the O_3 formation in the inflow air into St. Louis. If the values of one or more of these local meteorological parameters differ sufficiently between wind flow directions the differences in O_3 concentrations discussed in this work might be accounted for by such variations within the boundary layer rather than by variations in precursor concentrations.

In order to estimate the quantitative importance of the meteorological parameters on O_3 inflow concentration, a technique is needed capable of making quantitative adjustments in the O_3 inflow concentrations with variations in meteorological parameters. Such a technique was developed and is discussed in the Procedures section. The set of curves prepared relating O_3 inflow concentrations to meteorological parameters are used to adjust the monthly mean O_3 concentrations associated with the flow from one quadrant to the same values of the meteorological parameters associated with the flow from the other quadrant. The technique was applied to monthly mean O_3 inflow concentrations during the months of May–October for several pairs of wind flow quadrants

(Table 3). Monthly average O_3 concentrations provide a more severe test than do seasonal O_3 concentrations because the monthly average variations in the meteorological parameters between wind flow quadrants are larger. The monthly mean O_3 inflow concentrations for the pairs selected are consistently higher with wind flow from the NE or SE compared to the SW or NW and the differences in the means are statistically significant at $P \leqslant 0.10$.

The differences in the values in the meteorological parameters between quadrants are listed in Table 3, along with the observed and adjusted differences in monthly mean O_3 inflow concentrations. The adjustments are made for temperature and solar radiation intensity and for these two parameters and wind speed.

For cases 1, 4 and 7 the adjusted means in the inflow O_3 concentrations are only slightly smaller than the observed means. Six other cases not listed for which the observed means are not statistically significant also showed slight changes after adjustment of these meteorological parameters. The overall averages for the eight cases show only a 4-ppb adjustment which can be attributed to differences in temperatures and solar radiation intensities between quadrants. The larger decrease in the means when considering adjustments for wind speeds as well as temperatures and solar intensities are primarily associated with cases 2, 3 and 8. For these three cases, corrections for the lower wind speeds associated with inflows from the NE or SE appear to account for a substantial part of the observed differences in mean inflow O_3 concentrations.

It is not evident why lower wind speeds should be associated with increased O_3 concentrations in air parcels traveling over rural terrain, assuming low and relatively uniform emission rates for precursors. Air parcels traveling over such terrain should accumulate precursors at almost the same rate per unit of time irrespective of the wind speed.

It would be reasonable to assume that wind speed is actually serving as a surrogate for some other parameter. One such parameter is the mixing height. If mixing heights should vary directly with wind speeds, then smaller mixing volumes might possibly account for the higher O_3 concentrations associated with lower wind speeds. Precursors emitted into such smaller mixing volumes would accumulate to produce higher precursor concentrations with a greater potential to form O_3.

Maximum mixing height values usually are available during the RAPS study period on weekdays at one urban and one rural station (Schiermeier and Pooler, 1985, personal communication). A sufficient number of daily values of maximum mixing heights proved to be available for cases 1, 3, 5, 6 and 8 in Table 3. However, only in three out of ten of the comparisons (5 cases × 2 stations) are the means of maximum mixing heights smaller when the flow is from the NE or SE at lower wind speeds. For cases 3 and 8 which have the large adjustments for wind speed, only two out of four calculations indicate means of maximum mixing

Table 3. Differences in mean values of several meteorological parameters and inflow ozone concentrations between wind flow quadrants into St. Louis area

Case No.	Month	Year	Quadrants	Differences in mean values of met. parameters			Differences in mean O_3 inflow concn. (ppb)		
				Temp. (°C)	Solar rad. (ly m^{-2})	Wind speed (m s^{-1})	Obs.	Adj. (T,SR)	Adj. (T,SR,WS)
1.	May	1975	NE–SW	−5.5	+0.24	−0.9	+21*	+20	+17
2.	June	1975	NE–SW	−0.8	−0.01	−1.9	+26†	+28	+12
3.	July	1975	NE–SW	−0.1	+0.17	−1.3	+25*	+17	+3
4.	May	1976	SE–NW	+1.6	+0.13	−0.9	+21‡	+17	+17
5.	Sept.	1976	SE–NW	+3.1	+0.20	−0.8	+18*	+8	+8
6.	Oct.	1976	SE–NW	+3.7	+0.13	−0.6	+24†	+12	+12
7.	May	1976	SE–SW	+0.2	+0.07	−0.3	+17‡	+15	+15
8.	June	1976	SE–SW	−3.1	+0.11	−1.3	+19†	+16	+9
						avg.	+21	+17	+12

* $P \leqslant 0.02$, † $P \leqslant 0.10$, ‡ $P \leqslant 0.05$.

heights which are smaller when flow is from the NE or SE. Therefore, it was not possible to demonstrate a consistent direct relationship between maximum mixing heights and wind speeds.

Based on an examination of daily values of O_3, other pollutants such as particle S and meteorology, it appears that the slower wind speeds are most likely to be associated with the anticyclonic flows as warm high pressure systems move E. Therefore, the slower wind speeds are actually serving as a surrogate for higher loadings of O_3 precursors accumulated to the E and flowing into the St. Louis area.

CONCLUSIONS

Several results related to the effects of directionality on O_3 inflow concentrations usually can be associated with the following conditions: (1) E wind flows during the second and third quarters of the year, (2) SW wind flows relative to NW wind flows, (3) wind flow from the SE relative to the NE and from the SW relative to the NW during the first and fourth quarters of the year. Peak monthly mean O_3 inflow concentrations occur during the late spring and summer. The frequency with which daily average O_3 inflow concentrations, 1200–1500 h CST, at and above 80 ppb occur is much higher during these peak months and with the wind flow from the E.

During the warmer months of the year the observed inflow concentrations can be accounted for by varying contributions from a combination of processes. These processes include: (1) photochemical formation of O_3 within the planetary boundary layer from anthropogenic precursors, (2) photochemical formation of O_3 within the free troposphere and (3) transport of stratospheric O_3 to ground level.

Substantial increments in O_3 concentrations occur at rural sites E of St. Louis over those well to the W of St. Louis. It seems most likely that these increments can be best explained by O_3 formation from anthropogenic precursors within the planetary boundary layer, as well as in the lower free troposphere. In particular these increments can be associated with the higher O_3 concentrations generated on a regional scale with anticyclonic transport during the passage of warm high pressure systems across the midwestern U.S.

There is little available evidence to associate incremental O_3 concentrations with O_3 formation contributed to by biogenic HCs on a local scale. Contributions from O_3 formation during longer-range transport are limited by the short lifetimes of biogenic HCs.

Differences in the values of meteorological parameters between wind directions have the potential to cause effects on O_3 photochemical formation. However consideration of the effects of such differences in solar radiation intensities and temperature account for only a few ppb in inflow O_3 concentrations. Differences in wind speeds appear to be responsible for similar sized adjustments in O_3 concentrations. However variations in wind speed over rural terrain alone don't seem capable of explaining the calculated differences in O_3 concentrations. Differences in mixing volume might do so but no consistent relationships between wind speed and mixing height could be obtained. This leaves as a reasonable possibility that the lower wind speeds observed with easterly flows simply serve as surrogates for higher O_3 precursor concentrations.

Empirical calculations and modeling results provide estimates of the ppb of O_3 formed photochemically in the planetary boundary layer per ppb of NO_x. The ratios obtained indicate that rather small differences in NO_x concentrations, within observed concentration ranges, could account for the increments in O_3 concentration from W to E of St. Louis.

Disclaimer—Policy issues discussed and implied in this paper should not be construed to represent official Agency policy. Furthermore, mention of trade names or of commercial products does not constitute endorsement or recommendation for use.

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